

DESULFURIZATION OF MODEL OIL USING PYRIDINIUM-BASED IONIC LIQUID

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ABSTRACT

Sulfur is the most abundant element found in crude oil. This paper contains the study on desulfurization of model oil by extraction with Pyridinium-based ionic liquids. The objective of the project is to determine the sulfur compound, dibenzothiophene (DBT) removal efficiency of pyridinium-based ionic liquids, 1-ethylpyridinium ethylsulfate, (EpyESO4) from model oil. In order to characterize the Pyridinium-based ionic liquids, the characterization process of [EpyESO4] was conducted by using fourier transform infra-red (FTIR) analyzer. Lab testing on desulfurization has been done by using different concentration of DBT (100ppm and 1000ppm) at 10 minutes of extraction time. The efficiency of the removal process has been determined using high performance liquid chromatography (HPLC). From the result, [EpyESO4] shows high efficiency in remove aromatic sulfur compound (DBT) at low concentration of sulfur content. The percentage sulfur removal from the model oil for 100ppm and 1000ppm were, 97.68% and 26.68% respectively. By considering these results, [EpyESO4] might be used as promising solvents for the extractive desulfurization of diesel.

ABSTRAK

Sulfur adalah elemen yang paling banyak terdapat dalam minyak mentah. Kertas ini mengandung kajian mengenai nyahsulfur daripada model minyak melalui pengekstrakan oleh cecair ionik berasaskan Pyridinium. Objektif projek ini adalah untuk menentukan kecekapan penyingkiran komposisi sulfur, dibenzothiophene (DBT) oleh cecair ionik berasaskan Pyridinium, 1-ethylpyridinium ethylsulfate (EpyESO4) daripada minyak model. Dalam usaha untuk menentukan ciri-ciri cecair cecair ionik berasaskan Pyridinium, proses pencirian [EpyESO4] telah dijalankan dengan menggunakan penganalisis fourier transform infra-red (FTIR). Ujian makmal pada proses nyahsulfur telah dilakukan dengan menggunakan kepekatan DBT berbeza (100ppm dan 1000ppm) dengan tempoh pengakstrakan selama 10minit. Kecekapan proses penyingkiran telah ditentukan menggunakan High Performance Liquid Chromatography (HPLC). Berdasarkan keputusan yg diperoleh, [EpyESO4] menunjukkan kecekapan yang tinggi dalam menyingkirkan kompaun aromatik sulfur (DBT) pada kepekatan sulfur yang rendah. Peratusan penyingkiran sulfur daripada model minyak untuk 100ppm dan 1000ppm adalah, masing-masing 97,68% dan 26.68%. Dengan mengambil kira keputusan ini, [EpyESO4] boleh digunakan sebagai pelarut yang menjanjikan untuk desulfurization ekstraktif diesel.

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LIST OF ABBREVIATIONS

| | |
|----------------|--------------------------------|
| $C_{12}H_{23}$ | Chemical Formula |
| $C_{10}H_{20}$ | Chemical Formula |
| $C_{15}H_{28}$ | Chemical Formula |
| COS | Carbonyl Sulphide |
| EpyESO4 | 1-ethylpyridinium ethylsulfate |
| H_2S | Hydrogen Sulphide |
| H_2SO_4 | Sulphuric Acid |
| mm | millimeter |
| μm | micro meter |
| mL | milliliter |
| min | minute |
| ppm | Part per Million |
| SO_2 | Sulfur Dioxide |
| SO_3 | Sulfur Trioxide |

LIST OF ABBREVIATIONS

| | |
|-------|--|
| DBT | Dibenzothiophene |
| ILs | Ionic Liquids |
| MECA | Manufacture of Emission Controls Association |
| HDS | Hydrodesulfurization |
| FTIR | Fourier Transform Infrared |
| HPLC | High Performance Liquid Chromatograph |
| MBPD | million barrels per day |
| LPG | Liquefied Petroleum Gas |
| EIA | Energy Information Administration |
| IEA | International Energy Annual |
| AER | Annual Energy Review |
| US | United State |
| PM | Particulate Matter |
| TSILs | task-specific ionic liquids |

1 INTRODUCTION

1.1 Background of Study

Sulfur is an abundant and non-metal element. Numerous organic sulfur compounds are found in coal and crude oil (Yoshikazu et al, 1994). Sulfur in crude oil is organically bound and mainly in the form of condensed thiophenes where up to 70% of the sulfur found in petroleum are dibenzothiophene (DBT) and substituted DBTs (Mohammad et. al, 2010). In recent year, great attention has been paid to the deep desulfurization of fuel due its negative impact to the environment (Hongshuai et. al, 2008). Takashi et. al. (1996) identified combustion of sulfur in unprocessed fossil fuels lead to serious environmental problem of acid rain. Besides, sulfur in gasoline inhibits the emission control performance of catalyst technology (MECA, 1998).

Desulfurization is the term for process of remove sulfur compound. One of the conventional methods that widely used in industry to remove sulfur is hydrodesulfurization (HDS). Yet, this process require high temperature and pressure condition, high energy costs, and was found has difficulty to remove aromatic heterocyclic sulfur compounds such as dibenzothiophene (DBT) and its derivatives. So, the others method were proposed such as adsorption, biodesulfurization and extraction. In this research, the sulfur removal method is focusing on extraction by ionic liquid.

Ionic liquid has been said as green solvent for the future because the ionic liquid process does not require strictly anhydrous conditions or an inert atmosphere to carry out the reaction. This makes the whole reaction sequence easier, cheaper, and less time consuming to perform. According to Martyn J. and Kenneth R. (2000) by choosing the correct ionic liquid, high product yields can be obtained, and a reduced amount of waste can be produced in a given reaction. Often the ionic liquid can be recycled, and this leads to a reduction of the costs of the processes. It must be emphasized that reactions in ionic liquids are not difficult to perform and usually require no special apparatus or methodologies. The reactions are often quicker and easier to carry out than in conventional organic solvents.

1.2 Problem Statement

Sulphur has been claimed as one of the component in crude oil and was found in both gasoline and diesel. When those fuels are burned, sulfur is emitted as sulfur dioxide (SO₂) or sulfate particulate matter. Particulate matter in open air can cause serious air pollution if there is no prevention. In addition, SO₂ in engine can affect on the vehicle emission. According to Miłosław K. and Jerzy M. (2005) in their research, about 98% sulfur contained in diesel fuel is oxidized in the combustion process to SO₂ which together with exhaust gas is released to the atmosphere where it can be subject to other reactions contributing to the creation of London-type smog and acid rains. Acid rain or acid precipitation is defined as rainfall with a pH lower than 5.6. Acid rain can cause such big impact to the environment, plant, aquatic life and human as well. Then, United States, Europe and some Asian countries limit sulfur emissions for on-road diesel to 500 parts per million (ppm). In less developed areas of the world the maximum sulfur ranges from 2000 ppm to above 5000 ppm. According to Katherine (2009) in Sweden, concentration of sulfur in diesel should be 10 ppm sulfur has been commercially available for several years.

1.3 Research Objectives

The main objective of this study is to remove sulfur compound (DBT) from model oil by study the aromatic compound of the sulfur and ionic liquid used in the extraction process.

1.4 Scope of Research

The following are the scope of this research:

- i) To characterized ionic liquid, ILs using Fourier Transform Infrared (FTIR) analyzer
- ii) To remove sulphur compound, DBT from model oil by extraction at volume ratio of 1:1, 1:2, 1:3 and 1:4.
- iii) To study the effect of pyridinium-based ionic liquid on the percentage of sulfur removed by using High Performance Liquid Chromatography (HPLC).

1.5 Significant and Rationale

There are several significant of this study:

- Lower operating cost.
 - ILs can be prepared without required any modern technology and it can done using common chemical solution.
 - The energy cost for sulfur removal is less compare conventional HDS since it does not required high condition of temperature and pressure.
- Effective.
 - ILs can remove sulfur and has high ability to extract aromatic compound.
 - Easy to conduct.
 - Less time for sulfur removal process.
- Environmental friendly.
 - . ILs can be re-use again by purified the ILs by rotary evaporation.

2 LITERATURE REVIEW

2.1 Introduction

Petroleum diesel fuel commonly has chemical formula of $C_{12}H_{23}$, ranging approximately from $C_{10}H_{20}$ to $C_{15}H_{28}$. Composed from 75% of saturated hydrocarbon (primarily paraffins including n, iso and cyclo) and 25% of aromatic hydrocarbons (including naphthalenes and alkylbenzenes). The first refined product was kerosene which has been discovered in Pennsylvania in 1859. The development of the internal combustion engine began in the late eighteenth century by Rudolf Diesel on 1892 came out with a patent for a compression ignition reciprocating engine which used coal dust as fuel but it was useless. Later on, he found that diesel (byproduct liquid petroleum) might be better engine fuels than coal dust. Once fuel change, his mechanical design also changes and succeeds with his prototype engine in 1895. Until now, both engine and fuel used his name.

The demand for transportation fuels has been increasing in most countries for the past three decades (Chunshan, 2003). The total world petroleum consumption increased from 49.42 million barrels per day (MBPD) in 1971 to 77.12MBPD in 2001, representing a 56% increase (EIA/IEA, 2002). The total US consumption of petroleum products reached 19.59MBPD in 2001, about 39% increase from 1971 (14.11 MBPD). Of the petroleum products consumed in US in 2001, 8.59MBPD was supplied as motor gasoline, 3.82MBPD as distillate fuels, including 2.56MBPD as high-way diesel fuels and 1.26MBPD as off-road fuels and industrial fuels, 1.65MBPD as jet fuel, 0.93MBPD as residual fuel oil, and 1.13MBPD as liquefied petroleum gas (LPG), and 3.47MBPD for other uses in the US (EIA/AER, 2001).

2.2 Diesel Consumption

At first, diesels were used to power ships, trains and industrial plants. The uses began to increase from year to year until nowadays, diesel are widely used for many sector all over the world such as transportation, manufacturing, construction, farming and power generation (John et. Al., 2007).

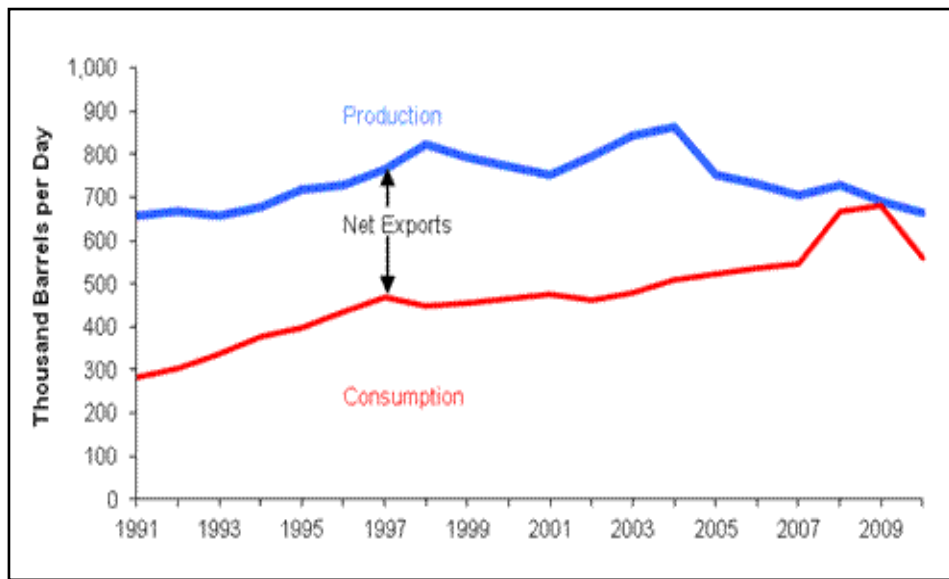


Figure 2-1: Malaysia's Oil Production and Consumption from 1991-2010
(Source: EIA)

From figure 2-1 we can see that the trend of oil consumption, increase from year 1991 to 2009 and a little bit decline on 2010.

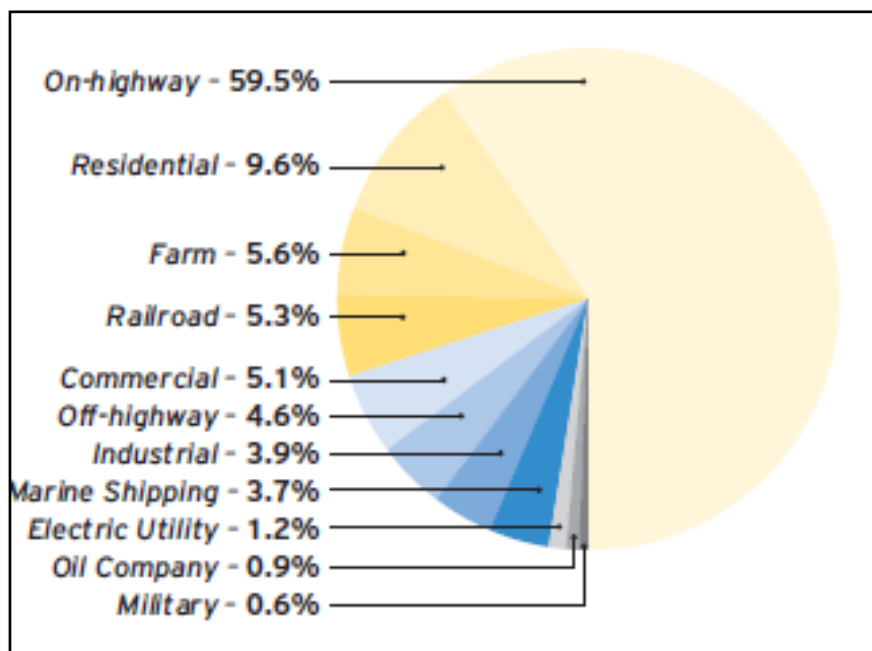


Figure 2-2: 2004 U.S. Diesel Fuel Sales According to Sector
(John et. Al, 2007)

Based on figure 2-2, on-highway transportation, primarily trucks, accounted for nearly 60 percent of the diesel fuel consumed in 2004 In the United States. Because diesel fuel is used to move goods from manufacturer to consumer, its sales are linked to the strength of the economy.

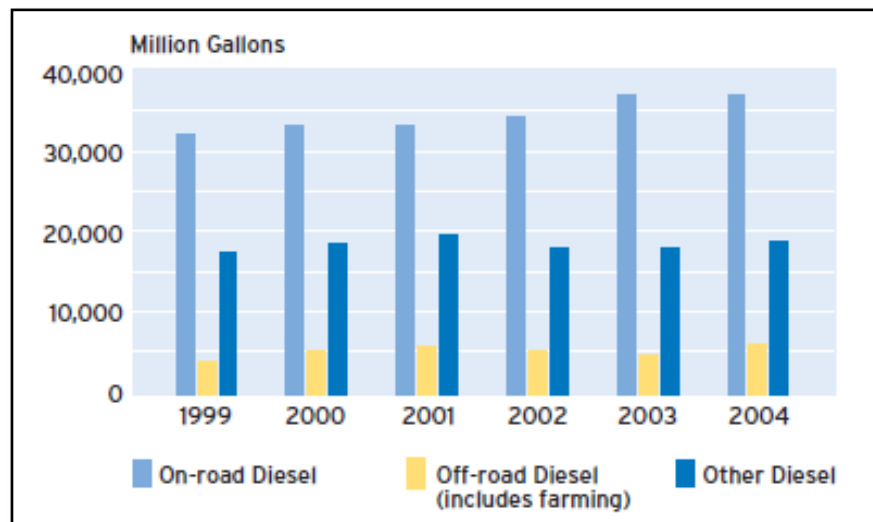


Figure 2-3: Trends in U.S. Diesel Fuel Sales 1999-2004

(Source: John et. al., 2007)

Figure 2-3 shows that sales of on-road diesel fuel in the U.S. raised from 32 billion gallons in 1999 to over 37 billion gallons in 2004, an increase of nearly three percent annually. By comparison, U.S. gasoline sales in 2003 were 136 billion gallons and jet fuel sales were 24 billion gallons. Most of the diesel fuel sold in the U.S. is refined in the U.S. Relatively small volumes are imported and exported in response to market conditions in coastal or border locations. The Energy Information Administration estimates that worldwide production of diesel fuel in 2002 was nearly 197 billion gallons.⁴ In Europe and Asia, where there is a significant population of diesel-powered automobiles the amount of diesel fuel produced exceeded the production of gasoline by just over 1.7 billion gallons.

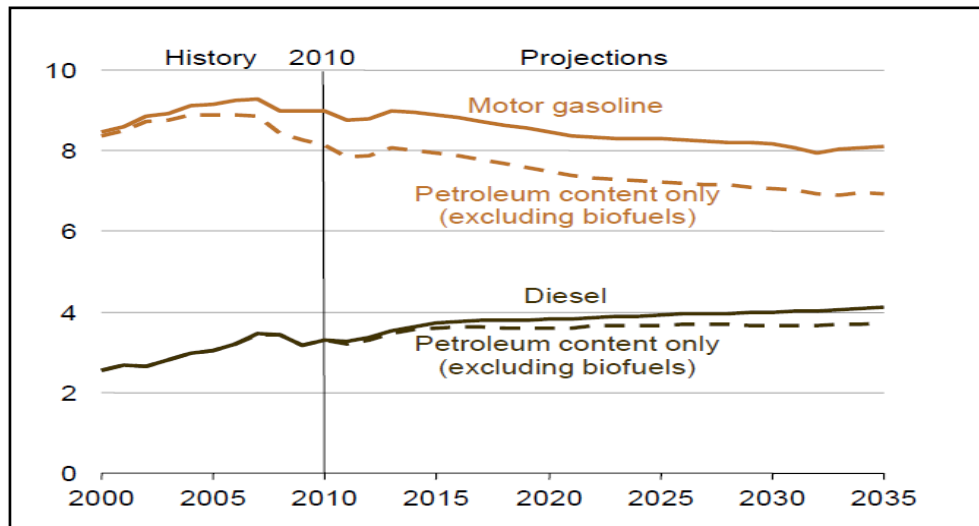


Figure 2-4: U.S. motor gasoline and diesel fuel consumption, 2000-2035 (MBPD)
(Source: EIA 2012)

From figure 2-4, we can observed that the consumption of diesel fuel in U.S. increases by approximately 0.8 million barrels per day from 2010 to 2035, while motor gasoline consumption falls by 0.9 million barrels per day.

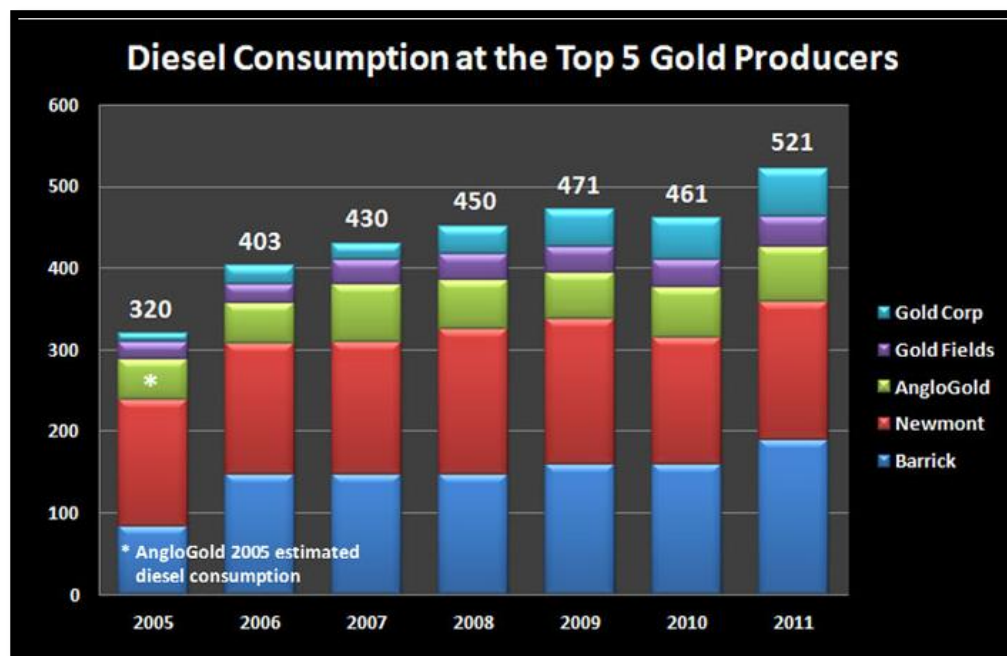


Figure 2-5: Diesel Consumption based on Top 5 Gold Producers
(Source: <http://www.silverbearcafe.com>)

Figure 2-5 shows the relationship between head grades and diesel consumption in these gold producers. Here we can see that the lower the head grade in the mining companies

reserves, the higher the amount of diesel is consumed. Newmont (shown in red in both charts) has the lowest head grade of the bunch, and it consumes the highest amount of diesel. On the other hand, Gold Fields (purple) has the highest average head grade and consumes the least amount of diesel. If we assume that GoldCorp's reserve head grade is similar to Newmonts, and it was producing the same amount of gold as Newmont, its overall diesel consumption would be more than twice of what it is currently.

According to their 2011 Annual Report, GoldCorp forecasts a 70% increase in gold production (1.75 million oz) in the next five years. If they are successful in bringing on this new production, it will increase in their diesel consumption from 58 million gallons in 2011, to nearly 100 million gallons by 2016. As ore grades decline more diesel is consumed in the mining process. Furthermore as open-pit mines age, it takes more energy (diesel) to extract the same or even less metal. In the past five years, the top 5 gold companies have increased their diesel consumption 72% per ounce of gold produced.

Based on the entire figure above, the consumption of diesel increases as time passes. It shows that if the diesel used contained a high amount of sulfur, the possibility of bad impact increases.

2.3 Sulfur

Sulfur is present in petroleum in a form of different compounds of which about 70% are made up by thiophene and its derivatives. The range of the sulfur is between 0.1 to 10% depending on a place of origin. (Miloslaw et. al, 2005). As the temperature of boiling point of individual fractions increases, the sulfur content in diesel fuel fraction increases.

Table 2-1: Properties table of Sulfur

| Physical Properties | Description |
|---------------------|--------------------------------|
| Atomic number | 16 |
| Atomic Mass | 32.06 g.mol ⁻¹ |
| Density | 2.07g.cm ⁻³ at 20°C |
| Melting Point | 113°C |
| Boiling Point | 445°C |
| Specific Gravity | 2.07 at 70°F |
| Solubility in Water | Insoluble |


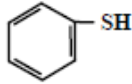
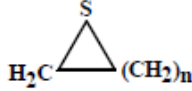
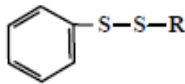
| Compound | Chemical formula |
|------------------------------|---|
| Hydrogen sulphide | H ₂ S |
| Thiophen and its derivatives |  |
| Aliphatic mercaptans | RSH |
| Aromatic mercaptans |  |
| Aliphatic sulphides | R-S-R |
| Cyclic sulphides |  |
| Aliphatic disulphides | R-S-S-R |
| Aromatic disulphides |  |
| Polysulphides | R-S _n -R |

Figure 2-6: Chemical Formula for certain Compound

(Source: Miloslaw et. al., 2005)

Formation of hydrogen sulphide H_2S is only occur when the rich air-fuel mixture is burned, whereas carbonyl sulphide COS appears at the exhaust gas temperature higher than $700^{\circ}C$. Certain Part of SO_2 in the presence of oxygen contained in exhaust gas can be oxidized to SO_3 . The high exhaust gas temperature causes that SO_3 remains in its vapour state and easily combines with water formed during the combustion process.

In the exothermic reaction the aerosol of sulphuric acid is formed, which with the chemically bonded water makes up one of the components of the particulate emission (PM). Certain amount of SO_3 being formed during the combustion process combines also with hydrocarbons or metals forming sulphates (chemical compounds containing SO_4^{2-} group, are called sulphates, including sulphuric acid H_2SO_4). Metals can come from the products of abrasive wear of the engine elements, from lubricating oil, fuel (catalyst residue) or erosion of exhaust system. In general, forming the sulphates requires SO_2 present in exhaust gas to be oxidized to SO_3 . However, under normal conditions (lack of catalyst) such a process proceeds very slowly and as a result of that only approx. 1% of SO_2 is oxidized before leaving the engine exhaust system (Kozak, 2000).

2.4 Effect of Sulfur in Diesel and Gasoline

2.4.1 Environment

According to Patrick et al., (1990) sulfur oxide contributed to environmental pollution problem such as acid rain. Takashi et al., (1996) also claimed that environmental problem of acid rain was cause by the combustion of sulfur compound in unprocessed fossil fuels. More researchers also claimed that those sulfur emission release to the environment contribute to acid rain and air pollution. Mohammad et al., (2010) highlight in their research that sulfur dioxide emission trough fossil fuel combustion isa major contributor to the generation of acid rain and air pollution.

2.4.2 Engine Performance

Sulfur compoud in fuel indicate corrosion to the parts of internal combustion engines due to the formation of oxyacid of sulfur from the product of combustion (Patrick et al., 1990). Thus, it will affect the performance of engine.

2.4.3 Human Health

Acid rain harms human through atmospheric and soil pollution. Acid rain causes formation of toxic compounds by reacting with naturally occurring chemical compounds. This toxic compound can be found in drinking water when the acid rain seeps into the soil and spreads to the source of drinking water and also the food chain. This contaminated food can damage nerves in children or result in severe brain damage and even worse can cause death. Scientists suspect that aluminium, one of the metals affected by acid rain, has a connection with Alzheimer's disease. The emissions of sulfur compounds cause serious human health and environmental concerns (Katherine et al, 2009). Sulfur dioxide can affect the breathing capacity of lungs and cause permanent damage to the lung.

2.4.4 Plant

When it rains, the water will absorb into the earth. The plant will be poisonous since it absorbs the toxic water from the soil which highly contains sulfur dioxide. This rain also dissolves the beneficial minerals and nutrients in the soil which are then washed away, before the plant has a chance of using them in order to grow. When there is frequent acid rain, it corrodes the waxy coating of the leaves. When the protective coating is lost, the plant will be easier to get diseased and can cause its death.

2.4.5 Aquatic life's

A high amount of sulfuric acid in the seawater will interfere with the ability of fish and other aquatic life to take nutrients, salt, and oxygen. Same as human, they need a balance amount of minerals and salts in their tissues. The molecules of acid result in mucus forming in their gills which prevents them from absorbing oxygen. Besides that, the acidity which results in reduced pH levels will cause an imbalance of salt in the tissues of fish body.

2.5 Ionic Liquids (ILs)

Ionic liquid is a liquid mainly consists of positively charged cation and a negatively charged anion. ILs are a class of ionic compounds in liquid state at room temperature. By having such great properties of thermal stability, negligible vapour pressure, miscibility, high conductivity and high capacity, ILs have gained good perception among the

researcher for their research since it has wide range applications in industry and give such no environmental effect.

The cation's structural factors are important in determining the physiochemical properties of the ionic liquid. These factors include symmetry, polarity or charge density, cyclic and branched structures, and the functional tail groups where any of these factors can be changed either singularly or in conjunction with other changes to vary the properties of the ionic liquid. The ability to change various factors of the cation and the selection of various anions allows for the variability of ionic liquids causing them to be deemed task-specific ionic liquids (TSILs), since they can be tuned and varied to meet the application's needs.

Advantages of ionic liquid:

- Easy separation
- Liquid over wide range of temperature
- Very low pressure
- Non-flammable substance
- High thermally stable
- High mechanically stable
- Electrochemically stable
- Low toxicity
- Non-volatility

2.6 Application of Ionic Liquids (ILs)

Ionic liquids have many uses for industrial and research usages. Table 2-2 summarized applications of ionic liquid.

Table 2-2: Application of ionic liquid

| application | description |
|------------------------------|--|
| Process technology | <ul style="list-style-type: none">• Deep desulfurization• Gas separation• Extractive distillation• Liquid-liquid extraction |
| Functional fluids | <ul style="list-style-type: none">• Hydraulics oil• Storage media for gases• Lubricants• Surfactant |
| Synthesis and catalyst | <ul style="list-style-type: none">• Enzyme reaction• Immobilization of catalyst• Nanoparticle synthesis• Solvent for organic reaction |
| Thermodynamic application | <ul style="list-style-type: none">• Thermal fluids• Phase changing material• Sorption cooling media |
| Electrochemical applications | <ul style="list-style-type: none">• Fuel cells• Metal deposition and metal finishing• Batteries• Dye sensitized solar cells• Sensor• Super capacitors |
| Analytics | <ul style="list-style-type: none">• Electrophoresis• Solvent for GC head space• Solvents for Karl-Fisher titration• Solvent for GC head space• Solvent for protein crystallization• Materials for GC column |

2.7 Other Method to Remove Sulfur

- ❖ Hydrodesulfurization
 - Remove sulfur by convert organic sulfur in the feed to hydrogen sulfide in the presence of a transition metal catalyst and hydrogen (Mohammad et. al., 2010). This technique is high in cost and energy intensive since it required high hydrogen pressure and temperature for greater efficiencies sulfur removal but this technique is not effective at removing polycyclic sulfur compound (Rhee et. al., 1998).
- ❖ Oxidative desulfurization
- ❖ Bio-desulfurization
- ❖ adsorptive desulfurization
- ❖ ultra deep desulfurization

3 MATERIALS AND METHODS

3.1 Material and Apparatus

The model oil used for this experiment is n-tetradecane since carbon chain of model oil should be enough to be like as a diesel and the sulfur representative is dibenzothiophene (DBT). All of the materials are provided by Chemical Engineering Laboratory of University Malaysia Pahang. The main equipments for this experiment are Fourier Transform Infrared Spectroscopy (FTIR) and High Performance Liquid Chromatography (HPLC).

Table 3-1: Properties table of n-tetradecane

| Physical Properties | Description |
|---------------------|------------------------------------|
| Molecular Formula | $C_{14}H_{30}$ |
| Molar Mass | $198.39 \text{ g.mol}^{-1}$ |
| Density | 0.767 g.cm^{-3} |
| Melting Point | 42.6°F |
| Boiling Point | 488.7°F at 760mmHg |
| Specific Gravity | 0.7628 at 68°F |
| Solubility in Water | Insoluble |

Table 3-2: Properties table of dibenzothiophene

| Physical Properties | Description |
|---------------------|---------------------------------|
| Molecular Formula | $C_{12}H_8S$ |
| Molar Mass | $184.26 \text{ g.mol}^{-1}$ |
| Density | 1.252 g.cm^{-3} |
| Melting Point | $97\text{-}100^{\circ}\text{C}$ |
| Boiling Point | 332°C |
| Solubility in Water | Insoluble |

3.2 Preparation of Model Oil

Model oil was prepared by dissolved 402mg of Dibenzothiopene (DBT) in 70mL n-tetradecane to form 1000ppm sulfur content in the model oil. Then it was diluted to 750ppm, 500ppm, 400ppm, 300ppm, 200ppm and 100ppm. The entire sample has been analyzed for calibration standard of this research and calibration data was summarized in table 3-3.

Table 3-3: Calibration Data

| Concentration (ppm) | Area (mAU*s) |
|---------------------|--------------|
| 100 | 6305.6 |
| 200 | 12914.2 |
| 300 | 19008.0 |
| 400 | 24500.1 |
| 500 | 28689.0 |
| 750 | 37122.8 |
| 1000 | 41814.8 |

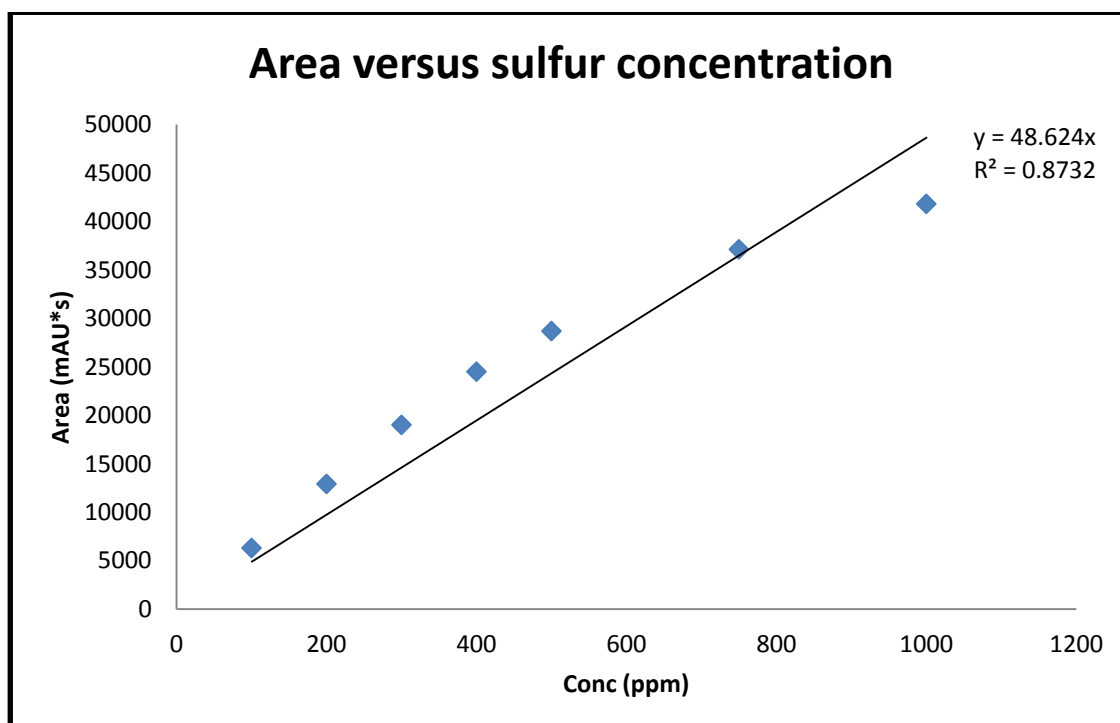


Figure 3-1: Standard Curve Graphs